

Remarks / Arguments

A request for continued examination (RCE) is submitted herewith.

The claims in the case at the time of the Final Action are canceled herewith. New claims 40-52 are submitted herewith. The Examiner at the interview of October 13 agreed to consider these new claims if an RCE was filed with the response.

Basis for new claim 40 is found in the application as filed at page 10, lines 19-21 taken with lines 1-3. Basis for new claims 41-43 is found in the application as filed at page 10, lines 19-21. Basis for new claims 44-47 is found in the application as filed at page 11, lines 6-10. Basis for new claim 48 is found in claim 1. Basis for new claim 49 is found in claims 3 and 12. Basis for new claim 51 is found in claim 4. Basis for new claim 52 is found in claim 10 taken with disclosure in the application as filed at page 5, line 27-30, page 6, lines 11-14 and 28 and page 22, line 32.

We turn now to the rejections based on Yasuda JP06-267544. Claims 1-12, 14-27, 29 and 31-39 are rejected under 35 U.S.C. 102(b) and 35 U.S.C. 103(a) over Yasuda. Claims 28 and 30 are rejected under 35 U.S.C. 103(a) over Yasuda taken with U.S. 5,298,350 and claim 28 is also rejected under 35 U.S.C. 103(a) over Yasuda taken with DE2758940.

Reconsideration is requested in view of the new set of claims submitted herewith, the Declaration under 37 C.F.R. 1.132 submitted herewith and the positions set forth below. The declaration is permitted in view of the RCE.

The new set of claims does not recite temperatures. Rather distinguishing features are levels of special grain boundaries (all claims), no increase in hardness

compared to before annealing (claims 44-47), deformed structure (claims 48-50), positive current collector, strap, lug or post (claim 51) and current collector (claim 52).

It is submitted that the recitation of special grain boundary levels in all claims distinguishes Yasuda and the combinations including Yasuda relied on in the Office Action.

This is firstly because of the showings set forth in paragraph 3 of the Declaration under 37 C.F.R.1.132 submitted herewith. These showings demonstrate that the only specific working example in Yasuda produces much less than 10% special grain boundaries, whereas the new claims require at least 20% special grain boundaries. This difference in special grain boundaries indicates better corrosion resistance for the claimed lead and lead alloys compared to the alloy prepared according to the only working example in Yasuda.

The difference in results between the claimed subject matter and the analysis data of the sole working example of Yasuda, is not surprising since the objectives of the invention and Yasuda are different. The purpose of the invention is to increase corrosion resistance of positive current collectors for use in a lead acid battery. On the other hand, Yasuda wants to improve paste - current collector grid adhesion and to increase the service life (better cycling) behavior of grid-paste interface due to presence of antimony; Yasuda is not concerned about the corrosion resistance of the current collector per se.

At the interview, the Examiner took the position that a showing based on Yasuda's sole working example, is insufficient because Yasuda's sole working example involves heat treating pasted plates at 60°C, whereas Yasuda's rolling at 120°C or less implies that his heat treating limitation of 60°C or higher encompasses heat treating at higher than 120°C (when rolling is at 120°C) where at least 20% special grain boundaries would be obtained.

The recitation of special grain boundary levels distinguishes Yasuda, secondly because the Examiner's position set forth in the above paragraph, is submitted to be wrong both on legal and substantiative grounds.

From a legal standpoint, it is submitted that Applicant's Declaration under 37 C.F.R. 1.132 meets the legal standard of comparison to the closest prior art. In the present case, the comparison standard is Yasuda. Yasuda has only one working example. Applicant's showing compares to the sole working example of Yasuda. It is submitted that applicant should not be required to pick and choose from Yasuda's general ranges including asserted implications thereof when the need for a certain level of grain boundaries is not disclosed in Yasuda, and Yasuda's purpose is satisfactorily met by his sole working example. Note also that implications and assumptions are inappropriate for anticipation rejections.

We turn now to the substantive reasons. It is submitted the Examiner's position on drawing an implication from Yasuda's 120°C rolling temperature limit, has to be incorrect. This is because Yasuda's heat treatment is carried out on pasted plate and heat treatment on pasted plates cannot be appropriately carried out above 66°C (see paragraph 5 of the Declaration under 37 C.F.R. 1.132). Otherwise the paste mass loses too much water. Heat treatment above the 66°C temperature, unfavorably influences paste density, paste workability, theoretical capacity and porosity, and causes change in plate color. Note that at 82°C, only 50% of the paste is converted to beta-PbO₂ which provides the useful discharge capacity. See paragraph 5 of the Declaration under 37 C.F.R.1.132. Note also that Yasuda's paste contains water per se and water from dilute sulfuric acid so that at 100°C, the water would boil off, changing the paste composition. Thus, the heat treating temperatures of Yasuda contended by the Examiner, cannot be the case.

The need for Yasuda to heat treat at 66°C or less as indicated above, apparently conflicts with Yasuda's cold rolling range. Applicant's should not be required to make a

showing encompassing this confusion or further limit its claims in view of this confusion.

If 66°C is considered as the upper heat treating limit for Yasuda, it is submitted that the showing at 60°C is sufficient. The law is that applicant gets credit for a reasonable range around the showing. There is no reason to conclude that results at 66°C would be significantly different from those at 60°C.

At the interview, at one point, the Examiner took the position, that Yasuda's working example had to include a heat treating step at a temperature above 120°, subsequent to the heat treating of the pasted plate at 60°C. There is no basis in Yasuda for this position. According to Yasuda, after filling the mesh with the paste, part of the grid recrystallizes in the heat treatment, which is defined as 60°C/48 hours. See [0021]: "Moreover, about the part, while the crystalline structure after sheet production had been in the condition of a rolling organization, expanded processing was performed, it was filled with paste, heat treatment of 48hrs was performed at 60C after that, and the organization of part of grid was made to recrystallize"(emphasis supplied). Yasuda provides direct evidence of the recrystallized grid after the 60C heat treatment in his Figure 3 as stated in paragraph [0025]. As Yasuda achieves his desired partial recrystallization at 60C/48hrs, there is no motivation for an additional heat treatment of Yasuda's pasted plate above 120C as asserted by the examiner and therefore no additional heat treatment is required or disclosed in his example. Moreover, the Declaration evidence indicates that Yasuda would not pursue this heat treating sequence of first heat treating at 60°C and then at 120°C, because of the severe detriments that would occur in Yasuda's pasted plates if this heat treating sequence were used.

Recognition that Yasuda does not impact Applicant's new set of claims, is requested.

Claims 1-12 and 14-39 have been rejected for obviousness type double patenting over U.S. Patent Nos. 6,086,691 and/or 6,342,110 and 6,592,686. Reconsideration is

requested. While claims 1-12 and 14-39 have been cancelled, terminal disclaimers are submitted herewith in anticipation of and to avert a double patenting rejection of claims 40-52.

Allowance is requested.

Respectfully submitted,
BACON & THOMAS PLLC

By: 

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Case: 6205

B&T Docket No. AUST3001 CIP

Date: October 18, 2004

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant : Gino Palumbo Confirmation No: 3992
Appl. No. : 09/991,702
Filed : November 26, 2001
TC/A.U. : 1742
Examiner : S. Ip

Docket No.: : AUST3001/JDB
Customer No: : 23364

DECLARATION UNDER 37 C.F.R. 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

We, Klaus Tomantschger and Peter Lin, hereby declare:

1. Klaus Tomantschger has a PhD in chemical engineering from Technical University Graz in Austria. He is presently vice president of intellectual property at Integran Technology.

2. Peter Lin has a PhD in metallurgy from the University of Toronto. His title is Project Engineer, Integran Technology.

3. Experiments were carried out under our supervision as follows. The experiments and results thereof are outlined in GBE Pb IP case (#6205) Support report of September 24, 2004, copy attached. The report also includes data (Results/Objective 3) of work carried out by Banner Power Company at our request in Linz, Austria. The results show heat treating at 60°C for 48 hours after cold rolling at 90% or 30% and in Banner's case at 60°C for 53 hours and 95% RH after cold rolling (85% deformation), provided Fsp content significantly less than 10%. The alloy for the first case was Pb-0.065Ca-1.4 Sn and in Banner's case Pb - 0.75Ca-1.35Sn. The results indicate much lower corrosion resistance than in the case of Fsp content of the invention.

Appl. No. 09/991,702
October 14, 2004

4. Experiments carried out by Banner at our request are described in a report titled "Heat treatment (GBE) of pasted plates after pasting and after curing" show heat treating at 295°C for 10 minutes after pasting caused incomplete conversion of paste (and therefore unacceptable paste product) and no mass grid adhesion (a requirement in Yasuda) and that heat treating at 60°C for 53 hours at 95% RH followed by 295°C for 10 minutes produced burning and weak plates, i.e. unacceptable plates.

5. Bode, John Wiley and Sons, 1977, copy attached, the bible for lead acid batteries, states at page 219: "Heat evolution occurs during the mixing process from mechanical friction and chemical reaction. Generally, cooling is necessary. The temperature of the paste should not exceed 65 to 70°C (see Sections 2.1 and 3.3 and Pierson, 1970). The mass loses too much water above this temperature so that paste density, paste workability, theoretical capacity, and porosity are influenced unfavorably." Pierson, J.R., Power Sources 2: Research and Development in Non-mechanical Electrical Power Sources: Proceedings of the 6th international Symposium - Brighton, September 1968 (1970 version referred to by Bode), copy attached, states at page 117 that curing above 66°C for pasted plates gives change in plate color and that at 82°C only 50% of the paste is converted to beta - PbO₂ which provides the useful discharge capacity. These results show that heat treating pasted plates in Yasuda's milieu at a temperature above 82° gives detrimental unacceptable results and conflicts with any conclusion that Yasuda allows for heat treating a pasted plate at a temperature greater than 82° and indicates that Yasuda cannot contemplate heating a pasted plate initially or after 60°C heat treatment, at 120°C or more.

6. That all statements made herein of our knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine of imprisonment, or both, under Section 1001 of Title 18 of the United States Code; and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Appl. No. 09/991,702
October 14, 2004


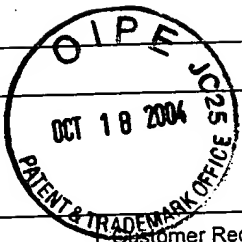
Oct 14, 2004
Date

Klaus Tomantschger
Klaus Tomantschger

Oct 14, 2004
Date

Peter Lin
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	GBE Pb IP Case (#6205) Support		
Project No: 2004-INT-503-0193	Customer Req. No.:	Date of Issue: Sep. 24, 2004	Page 1 of 3

BACKGROUND

The objective of this work was to provide experimental data for Integran's US Application 09/991,702 (#6205) to address the final rejection of July 26, 2004. Various tasks dealing with thermo-mechanical processing were performed using a lead alloy having a nominal composition of 0.065%Ca and 1.4%Sn which falls into the alloy range of Yasuda 0.05%-0.08%Ca and 0.5%-2%Sn and in composition is very similar to the Pb-0.070%Ca-1.0%Sn alloy Yasuda used in his example (which is laminated to a Pb-5.0%Sb-%5.0Sn alloy sheet). The Pb-Ca-Sn alloy was melted and held at 520°C for 20 minutes prior to casting. After processing OIM and hardness analysis was conducted. The first objective was to compare the effects of a paste drying treatment at 60 °C for 48 hours as disclosed by Yasuda with a GBE-anneal treatment as disclosed in US Application 09/991,702 (10min@250°C).

Processing matrix (objective 1):

- ☐ Cold rolling 90%
- ☐ Cold rolling 90% + heat treating @ 60°C for 48 hrs
- ☐ Cold rolling 90% + heat treating @ 250°C for 10 minutes
- ☐ Cold Rolling 30%+ heat treating @60°C for 48 hours
- ☐ Cold Rolling 30%+ heat treating @250for 10 minutes

The second objective involved heat treating a lead alloy having a nominal composition of 0.065%Ca and 1.4%Sn for 24 hours at 99°C which is below the minimum temperature specified in US Application 09/991,702 (>100 °C). This represents the highest temperature conceivable to heat-treat pasted plates at, although this treatment would result in pasted plates unsuitable for use in batteries.



Processing matrix (objective 2):

- ☐ Cold rolling 90%
- ☐ Cold rolling 90% + heat treating @ 99°C for 24 hrs

The third objective involved determining the Fsp count of the pasted and cured Banner plate (0.075%Ca and 1.3%Sn), which was not destroyed by a high temperature heat-treatment (see Banner Heat Treatment Report).

OIM Analysis of Banner pasted@cured grids (objective 3):

- ☐ Cold rolling 85% + heat treating @ 60°C for 53 hrs


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RESULTS/ Objective 1

Sample	Deformation [%]	Heat Treatment Temperature [°C]	Heat Treatment Duration	Fsp Count, [%]	Hardness [HV]
Control	90	N/A	N/A	<<10	12.2
#1a	90	60	48Hrs	<<10	19.7
#3a	90	250	10min	35	8.3
#1b	30	60	48Hrs	<<10	15.2
#2b	30	250	10min	37	7.5

ANALYSIS Objective 1

- (1) The OIM results indicate that the prolonged low temperature annealing treatment (60°C for 48hrs) of the deformed lead alloy (Pb-0.065Ca-1.4Sn) resulted in a Fsp count of less than 10% irrespective of the degree of prior deformation (i.e., 30% and 90%).
- (2) The high temperature annealing treatment of the deformed lead alloy resulted in a Fsp count in the range of 35-40% with a significant presence of $\Sigma 1$ -type grain boundaries.
- (3) The hardness of samples processed according to the patent specification (Fsp>20%) was lower than the hardness of the control while the hardness of samples processed according to Yasuda increased in hardness over the control.

			
	GBE Pb IP Case (#6205) Support		
Project No: 2004-INT-503-0193	Customer Req. No.:	Date of Issue: Sep. 24, 2004	Page 3 of 3

RESULTS/ Objective 2

Sample	Deformation [%]	Heat Treatment Temperature [°C]	Heat Treatment Duration	Fsp Count, [%]	Hardness [HV]
Control	90	N/A	N/A	<<10	12.2
#1c	90	99	24Hrs	<<10	14.4

ANALYSIS Objective 2

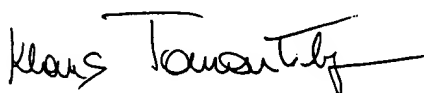
- (1) The OIM results indicate that annealing the deformed lead alloy (Pb-0.065Ca-1.4Sn) at 99°C for 24 hours yielded a Fsp count of less than 10%.
- (2) The hardness of the heat treated sample increased over the hardness of the control material due to age hardening.

RESULTS/ Objective 3


Sample	Deformation [%]	Heat Treatment Temperature [°C]	Heat Treatment Duration	Fsp Count, [%]
PC	85	60	53hrs	<<10

ANALYSIS Objective 3

- (3) The OIM results indicate that annealing the deformed lead alloy grid (Pb-0.075Ca-1.4Sn) after pasting and curing at 60°C for 53 hours yielded a Fsp count of less than 10%.



Dr. Klaus Tomantschger

 Protokoll am 07.09.04 - FEA THE POWER COMPANY		Verteiler nur zur Info.:
Betreff: Heat treatment (GBE) of pasted plates after pasting and after curing		Seite 1 von 2

Objective:

Evaluation of the influence of heat treatment (GBE 10 minutes @ 295°C) of pasted and pasted&cured positive expanded metal plates with Pb-Ca-Sn alloy grids.

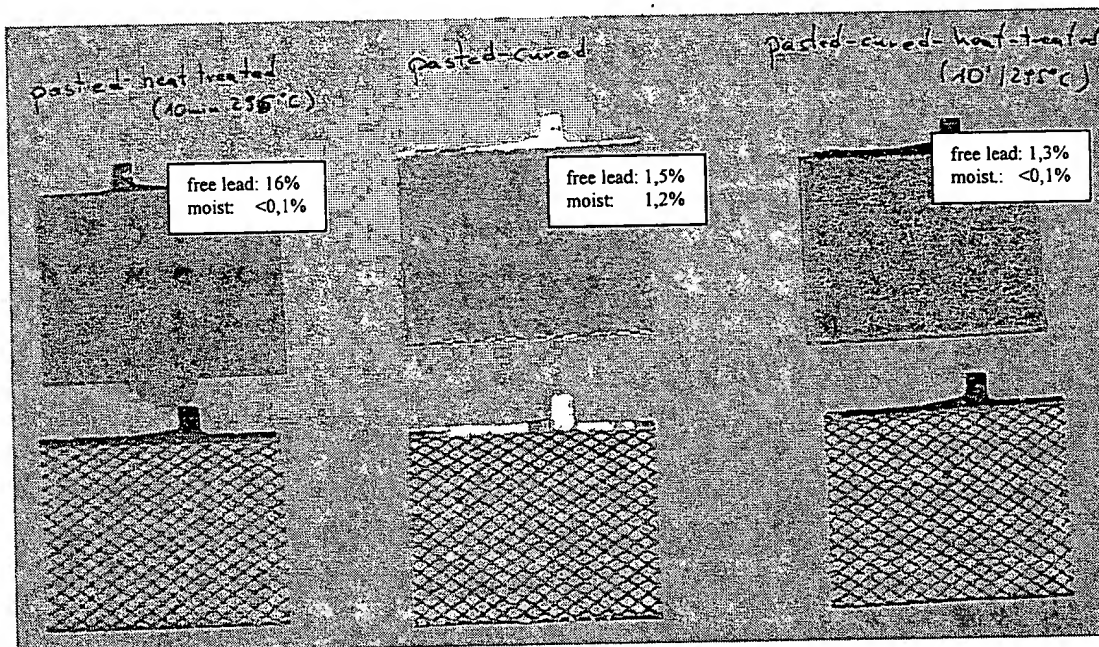
Test procedure:

- A 6.7 mm thick strip of a Pb-0.075Ca-1.3Sn alloy was cast and rolled to 1.0mm. The rolled strip was expanded to a mesh and pasted with active material.
- Take some plates direct after stacking (moisture appr. 9%) and heat treat these plates (10 min @ 295°C).
- Take some plates from the same rack after curing and heat treat these plates (10 min @ 295°C)
- Compare these plates with conventionally cured plates.
- Performance test, if possible.

Analysis:

- optical check (paper loss)
- mass grid adhesion
- free lead/moisture after treatment
- x-ray diffraction (crystal structure)

Documentation:



- no mass grid adhesion
- Paper loss due to heating
- almost no lead oxidation
- very weak plates

- standard, proper cured plates with good mass-grid adhesion and less free lead after curing

- black burning spots on paper surface
- no additional decrease of free lead due to heating procedure
- weak plates

Definitions:

P C	pasted and cured plates (53 hrs @ 60°C, 95% RH)
P HT	pasted and heat treated plates (10 min @ 295°C)
P C HT	pasted, cured (53 hrs @ 60°C, 95% RH) and heat treated plates (10 min @ 295°C)

X-ray analysis (crystal structure):

	P HT pasted heat treated	P C pasted cured	P C HT pasted cured and heat treated
PbO tetragonal red	ca. 77-80 %	ca. 80-82	ca. 80-82%
Tribasic lead sulphate	ca. 20 – 23 %	ca. 18 – 20%	ca. 18 – 20%
Tetrabasic lead sulph.	< 3%	< 3%	< 3%

No detection of tetrabasic lead sulphates due to heat treatment of the pasted plates (water evaporation during heat treatment is too fast to produce tetrabasic crystals → usually crystal growth is a very slow reaction which would need much moisture in the plates!!)

Conclusion:

- High temperature heat treatment of pasted plates shows almost no lead oxidation which should occur during the „standard“ curing process (spec. is less 2% free lead after curing).
- Very poor paper adhesion on the plates was also observed.
- Almost no mass-grid adhesion was noted.

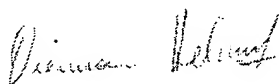
High temperature heat treatment of cured plates:

- High temperature heat treatment after curing results in dark burnt spots on the pasting paper.
- Plates/mass showed some cracks (expected to lower discharge capacity and cycle life).
- Very weak plates after heat treatment.
- High temperature heat-treatment of cured plates results in plates unsuitable for use in lead-acid batteries.

When subjected to a high temperature heat treatment (10 min @ 295°C) neither the pasted nor the pasted and cured positive grids have properties similar to standard cured positive electrode plates.

Due to the poor paste adhesion to the grid, the poor strength and cracking observed the plates exposed to a high temperature heat treatment could not be mounted in batteries and it is expected that the electrical performance including discharge capacity and cycle life will be very poor.

with kind regards,



Ing. Helmut Diermaier
R&D / Process Engineer Banner GmbH

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LEAD-ACID BATTERIES

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UNION CARBIDE CORPORATION

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The internal surface is dependent on the particle-size distribution, on the particle shape and on the oxide content.

3.3 PASTE PREPARATION AND CURING PROCESSES

In this section the relation between the characteristics of the lead dusts, the paste preparation, and the curing process are treated. Their relation to the electrical properties of the plates are discussed in Section 3.4.

To prepare a *formable* plate from lead dust a *pasteable* mass is prepared from air-dried powder with water and sulfuric acid applied to the active mass carrier (grid), and subsequently cured (see Section 2.6). In the dried plate the material must possess a certain dry strength so that it cannot fall out in the subsequent manufacturing procedures which, depending on formation, may differ.

Other characteristics that are important after conversion of the dusts and pastes into porous electrodes include the following

1. Porosity (overall value).
2. Pore distribution and average pore diameter.

In order to follow the preparation of plates from dust: it is assumed that a mixture (a heterogeneous multiple-phase system comprised additively of all components $1, \dots, i, \dots, l$) is present in all stages. Among the individual materials M_i^* of component i , the mole number n_i is obtained by dividing by the molecular weight M_i , $n_i = M_i^*/M_i$. For lead dust with the oxide weight fraction w_2 we obtain the number n_i of moles of metallic lead $n_1 = (1 - w_2)/207.19$ and n_2 of PbO , $n_2 = w_2/223.19$. If more components are added, an analogous calculation for every component applies.

If the sulfuric acid is converted to tribasic sulfate and the portion Δn_1 of the metallic lead is oxidized, the system consists of

$$\begin{aligned} & (n_1 - \Delta n_1) \text{ moles of lead} \\ & (n_2 - 4n_3 + \Delta n_1) \text{ moles of lead oxide} \\ & n_3 \text{ moles of tribasic sulfate} \\ & n_4 \text{ moles of water} \end{aligned}$$

If tetrabasic salt is formed, we find $(n_2 - 5n_3 + \Delta n_1)$ moles of oxide, n_3 moles of tetrabasic sulfate, and $(n_4 + n_3)$ moles of water.

These numbers permit the calculation of a series of properties of the paste or the system:

1. The total material from the molecular weights.
2. The total volumes from the molar volumes.
3. The density for (1) to (2).

4. The total heat capacities from the molar heat capacities
5. The specific heat from (1) and (4).

Likewise, the contribution of the individual components to the total volume, the total heat capacity, and so on, can be found.

If the material contains n_1 mole of metallic lead and n_2 moles of lead compounds, the theoretical Ah capacity is given by $2F(n_1 + n_2)$ or $(n_1 + n_2)(53.6)$ Ah. Dividing by total mass or volume, we obtain the specific capacity. The molar values of components of active materials in the lead storage battery are listed in Table 2.4.

MANUFACTURING PROCEDURES

As in all manufacturing procedures, we can distinguish discontinuous and continuous processes in which, in the trend of automation, continuous processes become significant when combined with proper control procedures.

The discontinuously operating mixing and kneading machines (capacity between 300 and 1200 kg of powder) have a mix-feed container of cast iron or acid-resistant steel. The blades for working the material may operate horizontally or vertically. The removal of the finished mass is accomplished by tilting the container or by opening the bottom.

The paste consistency depends on the manner of loading the mixer. If the dust is loaded first, water and acid may be added in various ways (Table 3.3).

In all cases the same paste density is attained, aside from water loss by vaporization, but consistency and plasticity may vary over a wide range. For the same mixing ratios (the same total amounts of water and sulfuric acid) the dust is treated with dilute acid before the remaining water is added. This procedure produces masses with the best plastic properties. If a concentrated acid is added first, hard grainy mixtures form. The lead sulfate formed because of localized enrichment in sulfuric acid converts with difficulty to basic lead sulfate in the brief mixing period. The paste should have a crisp, crunchy consistency, not creamy, sticky, or salvelike.

The relationships are similar if the loading of the mixer starts with water and sulfuric acid. Dust may be added to the most dilute acid; more uniform and better plastic masses are produced if only part of the water is mixed with the powder and the acid is added as the last component. The acid concentration is carefully selected so that the required amount is attained. Fibers (mostly dynel) are added for positive plates during the production process for the purpose of increasing their strength and reducing mud formation.

Some additives are required for negative plates. A dry premix is prepared with part of the dust and additive which is fed in suspension to the rest of

the mix in the mixer. The additive may also be added dry to an otherwise finished paste.

Heat evolution occurs during the mixing process from mechanical friction and chemical reaction. Generally, cooling is necessary. The temperature of the paste should not exceed 65 to 70°C (see Sections 2.1 and 3.3 and Pierson, 1970). The mass loses too much water above this temperature so that paste density, paste workability, theoretical capacity, and porosity are influenced unfavorably.

Cooling can be done with coils or jackets. In cooling by blowing air, heat is removed by the evaporation of water from the paste but additional heat is produced simultaneously because of the intensified oxidation. In the batch process a certain amount of cooling occurs during the unloading and during cleaning of the machine.

The mixer also kneads the active masses. For all machines in use a completely uniform distribution of the components is attained in about 15 to 30 minutes.

For continuously operating machines the same principles apply. Good heat transfer must be provided, for the closed structure prevents cooling by evaporation and during unloading. Because the evaporation of water is suppressed, more uniform pastes can be expected. Scales and metering devices are required for the loading and discharging of the mixers, manually or automatically, on a predetermined schedule. Temperature control is essential. Control of manufacturing occurs mainly by measuring the paste density (cube density), which provides control of the prescribed water content of the paste for a similar dust and constant sulfuric acid content.

The paste density must be controlled, for it determines the theoretical input and useful capacity through the porosity of the plates. Whatever paste density must be maintained, it depends primarily on the dust and mixing instructions and the type of pasting machine.

The finished pastes are fed to pasting machines in which the grids are automatically loaded or "pasted." Pasting by hand is done only in special cases. The pasting machines have a station for grid loading, a device for separating the grids, which are loaded in stacks, transfer devices for grids and masses, a mass container with the pasting devices, and a dimensional control device for the plate thickness, and a conveyor line for the pasted, still wet plates.

The following machine designs can be differentiated:

1. The position of the grid under the pasting tool; lengthwise, crosswise, or round table pasting machines.
2. The spatial position of the grid; horizontal or vertical pasting machines.

* All pastes contain 62 g H₂SO₄.

Paste No.	1	2	3	4	5	6	7
Water: Amount, cm ³	115	28	1.0	—	173	60	—
Time, min	—	—	—	—	2.2	1.0	—
Acid: Density, kg/liter	1.152	1.283	1.283	1.283	1.473	1.473	1.473
Amount, cm ³	244	130	130	130	73.8	73.8	73.8
Time, min	23.5	4.7	4.7	4.7	2.3	2.3	2.3
Water: Amount, cm ³	—	—	55	115	—	113.1	173
Time, min	—	—	1.0	2.5	—	1.0	1.2
Mixing Time, min	35	30	35	30	30	30	30
Temperature (maximum), °C	46.5	52	50	58	47	53	63
Total heat, kJ	111.5	109.0	124.0	112.0	113.0	129.0	128.0
Fractional heat	82.5	73.5	86.5	72.0	61.5	73.5	67.0
Chemical heat	29.0	35.5	37.5	40.0	51.5	55.5	61.0
Heat of dilution	0	3.0	3.0	3.0	10.5	10.5	10.5
Reaction heat	29.0	32.5	34.5	37.0	41.0	45.0	50.5
Paste density, kg/liter	3.60	3.54	3.54	3.57	3.47	3.60	3.60
Quality of paste	Very good	Good	Good	Sandy	Good	Sandy	Dead, sandy

TABLE 3.3. INFLUENCE OF THE ORDER OF MIXING ON THE QUALITY OF A PASTE* (EAGLE-PICHER, 1964).

3. The number and arrangement of pasting tools: one-sided or two-sided pasting machines.
4. The method of feeding the active mass: machines with blades and disks or rolls.
5. The method of transporting the grids: machines with conveyor, chains, or rolls or with templates to pick up the grid.

The machines can be equipped for calibration of the unpasted grid with stationary or rotating cutting tools. After pasting the material into the grid, the plates move to a rolling mill with adjustable separation for smoothing the two surfaces with stripping plates or other sizing devices.

For machines operating from both sides the material is pressed harder so that the mass loses water and the surface becomes smoother and denser than the interior. This process makes it more difficult to obtain uniform and crackfree shrinkage and the oxidation of metallic lead during the subsequent curing process. Pasting machines operating on one side press to a nearly constant water content and achieve more uniform porosity. This facilitates the "ideal" shrinkage process required for crackfree drying and the oxidation of lead.

The curing process consists of the conversion of wet pasted plates to a dry, crackfree, unformed plate of sufficient strength (dry strength) and adhesion to the grid. During this process two steps proceed simultaneously and in sequence (see Section 2.6):

1. Water loss by shrinkage.
2. Void formation.

Curing is an important part of manufacturing, for if it is not properly carried out capacity and especially life expectancy are adversely influenced. The curing can be done in different ways.

1. The plates are suspended individually on racks with small separations. According to a pre-established program, the plates are subjected to a flow of damp or dry air and finally heated. The curing and drying lasts about 16 to 24 hours.
2. The plates are hung on chains and moved through a tunnel kiln in which temperature is increased and humidity is decreased. The kiln is usually heated with CO₂-containing combustion gas which passes through the kiln.
3. The plates are flash-dried by gas heating or infrared heating so that they may be packed densely 20 to 30 cm high without sticking. They are covered

to prevent the process from proceeding too rapidly. Otherwise small cracks will appear. For oxidation and drying in stacks 4 to 6 days are required.

4. The plates are dipped in sulfuric acid or sprayed with sulfuric acid to form a dense lead sulfate film on the surface (pickling), a process frequently used for tubular plates (see Section 3.4) but less often for grid plates. For grid plates the formation of cracks on drying is retarded by treatment with dilute sulfuric acid. The related curing and drying is then carried out by procedure 1 or 3.

After curing the paste in the plates must have sufficient dry strength and adequate adhesion to the grid so that it does not detach during subsequent manufacturing steps and retains electrical contact with the grid during formation.

The plates obtained by proper curing can be handled without creating problems in the subsequent processing steps, are almost entirely free of metallic lead, and can be stored indefinitely in this state. In principle, damp plates may be formed immediately.

CHEMICAL PROCESSES

Lead dust mixed with water reaches a slightly alkaline pH value of about 9. Mill dust contains tetragonal PbO exclusively, whereas thermal dusts also contain rhombic PbO (up to 10% by weight). Occasionally some minium is found, sometimes added intentionally. Rhombic PbO, as the unstable modification, reacts preferably with sulfuric acid.

The amount of sulfuric acid added during mixing is not large enough to form neutral or monobasic sulfate. These two substances can form only when rapid addition, without sufficient stirring, causes localized high concentrations of sulfuric acid. Slower addition and vigorous mixing produce only higher basic sulfates. In the pH range in which the paste is in equilibrium with lead oxide only tribasic and tetrabasic sulfate form. Here temperature and amount of acid are significant.

At low temperatures and with the usual amount of acid tribasic sulfate results. It should decompose at 100°C but absorbs additional PbO and releases water above 70°C whenever the temperature in the paste rises sufficiently over long periods. This process occurs not only during mixing but also on curing in drying ovens and perhaps even during formation. Active materials with appreciable portions of tetrabasic sulfate are difficult to form according to Ikari et al. (1959) and Pierson (1970) and tend to form sludge. The mixing and curing processes must be carried out so that only tribasic sulfate will form (see Figure 3.6).



Figure 3.6 Electron microscope picture of the surface of a pasted plate *before* curing, enlargement 1:23,200 (Courtesy of ESB Inc.).

Lead paste always contains unchanged oxide, for the metallic lead is slowly oxidized during all mixing and curing processes. Also white hydrate and rhombic oxide can form (see Section 2.1). At the completion of the curing process the Pb must be oxidized until the residue is smaller than 5%. A Pb content of more than 5% is supposed to cause difficulties during the formation of positive plates (swelling or warping or extensive sludge formation).

During the initial stages of the formation of sulfate the components are often not identifiable by X-rays. At first crystal seeds are produced in sizes smaller than 10 nm which are X-ray amorphous. The strongly characteristic X-ray lines of tribasic sulfate appear later after recrystallization, a process (ripening) that continues in tribasic sulfate during curing until the crystallites can be seen optically and the submicroscopic and colloidal particles have almost disappeared. On conclusion of the process needleshaped crystals



Figure 3.7 Electron microscope picture of the surface of a pasted plate *after* curing, enlargement 1:23,200 (courtesy of ESB Inc.).

of 1 μ m thickness and several μ m in length may be found [see Figures 3.6 to 3.8, Mrgudich (1942); Sections 2.6 and 2.7].

After the mixing process a paste contains the following solid components: unchanged (tetragonal) and freshly formed (rhombic) lead oxide, tribasic sulfate as the component containing the added sulfuric acid, and finally some metallic lead the amount of which is decreased in comparison to the starting value. Added minium is not changed by mixing, for the process proceeds in an alkaline medium unless localized overacidification occurs. After curing the crystals are generally better formed and the metallic lead is oxidized to a small "residual lead content."

The formation of basic lead carbonate occurs as a side reaction. It is not detectable in the mass before pasting. On the other hand, the surfaces of the pasted plates contain larger amounts of carbonate. During absorption of

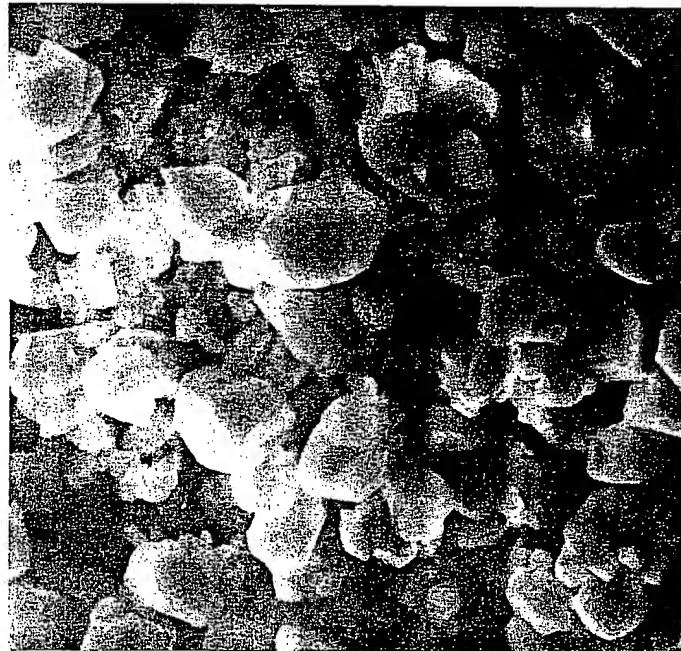


Figure 3.8 Stereo scan picture of the surface of an unformed negative plate; enlargement 1:4600 (G. Stier, 1970).

CO_2 water is also bonded because basic lead carbonate, $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$, causes the plate surfaces to dry rapidly, thus facilitating their stacking without sticking. Carbonate impedes formation, however. A small carbonate content may still be determined in the plates after many cycles.

HEAT EFFECT IN THE MANUFACTURE OF MIXTURES

The temperature in the mixing process affects the composition in the mixture. The undesirable formation of tetrabasic lead sulfate begins above 70°C . An increase in temperature can occur as a result of enthalpy changes in the chemical reactions as well as frictional heat [see Gillibrand and Wilde (1964)].

The assumptions for the calculation of a maximum temperature contain several factors, in particular, production variables that can only be approximate. For this reason several simplifications that do not substantially affect

TABLE 3.4. ENTHALPY OF NEUTRALIZATION OF PbO WITH H_2SO_4^a

Molality m_2 (mole/kg)	100 H_2O Mass (%)	Density ρ (kg/liter)	Neutralization Enthalpy ΔH_N (kJ/mole)
11.101	52.20	1.411	-133.96
5.551	35.20	1.258	-117.01
3.700	26.62	1.183	-113.13
2.221	17.82	1.113	-103.77
1.110	9.82	1.063	-101.32
0.50	4.85	1.029	-100.32

^a See assumptions in the text.

the results are introduced in the chemical reactions. There are three principal chemical reactions: oxidation of metallic lead; neutralization of lead oxide with sulfuric acid; and formation of hydroxides or hydrates.

The enthalpy change for oxidation of lead under standard conditions may be found in Tables IV to VI in the Appendix.

$$\Delta H_B^\circ = -219 \text{ kJ/mole or } -982 \text{ kJ/kg lead oxide}$$

This value, with the opposite sign, the heat of reaction, is exact only if tetragonal oxide forms. When unstable rhombic modification forms, the somewhat smaller value of -217.3 kJ/mole applies. This difference is neglected in the following. Among the possible neutralization reactions, only the formation of neutral lead sulfate, which includes the assumption that the enthalpies of formation of the basic sulfate are additively composed from its components, is considered. The enthalpy of neutralization depends on the concentration m_2 of sulfuric acid. The values are listed in Table 3.4.

The enthalpy of neutralization is eliminated entirely or in part if presulfated oxide is used (see Section 3.2).

Even when pure water is added to lead dust, there is always a small heating effect. In this case it is not the formation of hydroxides; it apparently arises from the heat of wetting which is not known for the system, lead oxide/water. The amount can be neglected if the surface areas are of the order of magnitude of several m^2/g and the heat of wetting is at 4 kJ/kg as in other materials with analogous specific internal surfaces [see Gregg (1958)].

The change in enthalpy may be estimated under simplifying assumptions; for example, when Δn_1 mole of lead is oxidized, n_3 mole of lead sulfate is formed. The heat capacity can be calculated (see Table 3.5) from the composition on completion of mixing. Three numerical examples should illustrate the effects of various important parameters. For 100 kg of lead dust with 65%

TABLE 3.5. NOTATIONS FOR CALCULATIONS OF THE CHEMICAL HEAT EFFECTS OF MIXTURES OF LEAD DUST, WATER AND SULFURIC ACID: COMPOSITION IN MOLES

Material	Initial State	Change	Final State	Enthalpy (kJ)	Heat Capacity (J/°C)
Lead	n_1	$-\Delta n_1$	$n_1 - \Delta n_1$	$\Delta n_1 \cdot 219.0$	$26.44 \cdot (n_1 - \Delta n_1)$
Lead oxide	n_2	$+\Delta n_1 - n_3$	$n_2 + \Delta n_1 - n_3$	—	$45.82 \cdot (\Delta n_1 + n_2 - n_3)$
Sulfuric acid and lead sulfate	n_3	0	n_3	$n_3 \cdot \Delta H_N$	$103.7 \cdot n_3$
Water	n_4	$+n_3$	$n_4 + n_3$	—	$75.29 \cdot (n_3 + n_4)$

PASTE PREPARATION AND CURING PROCESSES

TABLE 3.6. HEAT EFFECTS FOR THREE EXAMPLES GIVEN IN THE TEXT

Material	Mixture 1		Mixture 2		Mixtures 1 and 2		Mixture 3	
	Enthalpy (kJ)	Heat Capacity (kJ/°C)	Enthalpy (kJ)	Heat Capacity (kJ/°C)	Enthalpy (kJ)	Heat Capacity (kJ/°C)	Enthalpy (kJ)	Heat Capacity (kJ/°C)
Lead	5,250	3.8	5,250	3.8	5,250	3.8	5,250	3.8
Lead oxide	—	12.2	—	12.2	—	12.2	—	12.2
Lead sulfate	6,830	5.3	5,360	5.3	2,070	2.1	2,070	2.1
Water	—	87.6	—	87.6	—	87.6	—	87.6
Heat of reaction and heat capacity of the chemical components	12,080	108.9	10,610	108.9	7,320	98.4	7,320	98.4
Mechanically produced heat and heat capacity of the mixtures	1,400	15	1,400	15	1,400	15	1,400	15
Total heat and heat capacity	13.5 MJ	12.0 MJ/°C	12.0 MJ	0.12 MJ/°C	87 MJ	0.11 MJ/°C	87 MJ	0.11 MJ/°C

oxide content ($n_1 = 169$ mole Pb and $n_2 = 291$ mole PbO) the lead content is expected to decrease during mixing by $\Delta n_1 = -24$ to $n_1 = 145$. The dust is mixed in three different acid formulations (Table 3.6).

1. With 5 kg sulfuric acid ($n_3 = 51$) and 20 kg water ($n_4 = 1.110$). These components are added separately as 9.57 kg = 6.78 liter of sulfuric acid ($\rho = 1.411$) kg/liter and 15.43 liter of water.
2. With 5 kg sulfuric acid ($n_3 = 51$) premixed with 20 kg of water. The 25 kg of the diluted acid with a density $\rho = 1.127$ kg/liter is added.
3. With 2 kg sulfuric acid ($n_3 = 20.4$) premixed with 18.4 kg of water ($n_4 = 1.020$). It is added as 20.4 kg dilute acid with a density $\rho = 1.063$ kg/liter.

Estimation of the heat generated during the mechanical mixing is generally not possible. If the mixer motor is connected to a wattmeter, an estimate of the frictional heat may be obtained. The energy consumed in operating the mixer, either empty or filled with dry dust, appears to be about the same. It contributes only slightly to heating the load and covers the transmission and bearing losses. During the actual mixing period of about 2 to 5 minutes, when the mass is still very stiff, the additional energy is converted to heat. The value decreases into a small, approximately constant value for the finished paste. A mixer with a capacity of about 600 to 700 kg of powder

dust may introduce work equal to 2.5 kWh for each 600-kg load, or about 1400 kJ/100 kg of powder.

The chemically and mechanically generated heat is reduced by heat losses from

1. Vaporization of water.
2. Heat loss to the mixer and surroundings by conduction; the mixer may or may not be equipped with water or air cooling.

Chemical and mechanical heat is absorbed primarily by the mass and causes its temperature to rise, for heat conduction through the mass is minimal. Heat transfer to the mixer occurs mainly by direct contact. Temperature equilibrium can scarcely be attained in the mixing period of approximately 25 to 30 minutes. Yet a certain portion of the heat is transferred to the stirrer and a portion to the walls. Because the mass of the mixer is 200 to 250 kg, the mixer's heat capacity amounts to about 100 kJ/°C or proportionately about 15 kJ/°C for 100 kg of dust.

At the start of mixing the generated heat leads to a temperature rise in the mass accompanied by vaporization of water. The vaporization of water removes about 2400 kJ/kg of water evaporated at 45°C and a vapor pressure of water of 0.1 bar. In the evaporation of 1 liter of water/100 kg of powder the temperature lowers about 20 to 25°C (based on a heat capacity of 100 kJ/°C).

The oxidation of lead dust occurs from the very beginning of the mixing process. The reaction enthalpy of 5250 kJ/100 kg of powder could lead to a temperature rise, $\Delta T = 50^\circ\text{C}$ (or about $2^\circ\text{C}/\text{min}$), based on the estimated heat capacity of the material of about 100 kJ/°C, not considering heat transfer of the stirrer absorbs a portion. Oxidation does not occur in lead-free powders or in closed, continuously operating mixers.

If sulfuric acid is added continuously to mixtures 2 and 3 and no heat is lost to the mixer, mixture 2 is raised about 110°C and mixture 3, about 90°C . If a partial heat loss is assumed during a mixing period of 30 minutes, lower rises are estimated to be 3.0 to $3.5^\circ\text{C}/\text{min}$. In production the rise is usually less.

If during the mixing step a powder/water mixture is prepared first and the entire amount of high density acid is added within a few minutes, the temperature rise will be very rapid. For mixture 1, neglecting the oxidation of lead and without heat transfer to the mixer, a temperature rise of 60°C could occur in about 3 minutes. During admixing of sulfuric acid the product changes from a stiff powder/water mixture to a pasty sulfate. Because of the consumption of mechanical work required for kneading, the temperature increases above the calculated value. If equilibrium among all heat effects is attained (i.e., without additional cooling or evaporation of water), the temperature increase will still be above 70°C , which is usually considered to

be the critical temperature. Despite a considerable uncertainty in this estimate, we realize that mixtures with higher sulfate contents require additional cooling.

RHEOLOGY OF THE PREPARATION OF PASTED PLATES

The theoretical foundations were discussed in Section 2.6. The starting product for the manufacture of pasted plates is a lead dust. Its chemical composition should be considered insignificant at first. For dusts with or without lead similar observations apply with respect to mixing and curing, aside from the thorough oxidation of the metallic lead during the last stage of curing.

Lead powders are characterized by their water absorption by which the density is measured as a function of the addition of water (see Figures 2.56 to 2.58). Initially the density rises almost linearly. After a definite amount of water addition, characteristic of the powder, it rises steeply, attains a maximum, and then decreases. During this sequence the plastic state is achieved and traversed.

In the plastic range the particles are separated by a thin film of water which allows them independent movement. However, the particles must adhere to one another; therefore the water film must not be too thick. In this process an important part is assigned to the internal surface and especially to the portion of the particles sized below $1\ \mu\text{m}$. Systematic studies in this field are not available. Several known observations relate to the behavior of sulfate-containing mixtures (Burbank and Ritchie, 1969), during the curing and drying processes, as well as during formation. According to these results, the fine portion should be between 4 and 25%, but no studies have yet been devoted to the optimization of mixing formulations.

In Section 2.6 only mixtures of lead dust and water were discussed. The general rheological fundamentals are independent of the nature of the material. By the addition of sulfuric acid an appreciable portion of the oxide component is converted mainly into an anisotropic, needleshaped reaction product which forms slowly from the initial crystal seeds. The recrystallization continues, after mixing, during the curing process. The needle crystals make the packing bulkier. As the void volume gets larger, the strength increases. Figures 3.9 and 3.10 show the apparent density as a function of sulfate content and water addition. It is also shown that a change in the density of the solid (a function of sulfuric acid content) exerts a smaller effect on paste density than a change in the amount of water.

Figure 3.10 illustrates the dependence of the density maximum on the amount of sulfate for the two powders (1 + 2 in Figure 2.58) as well as the beginning of the plastic range. The water values of the density maxima shift to higher values with increasing sulfate content and additional amounts of

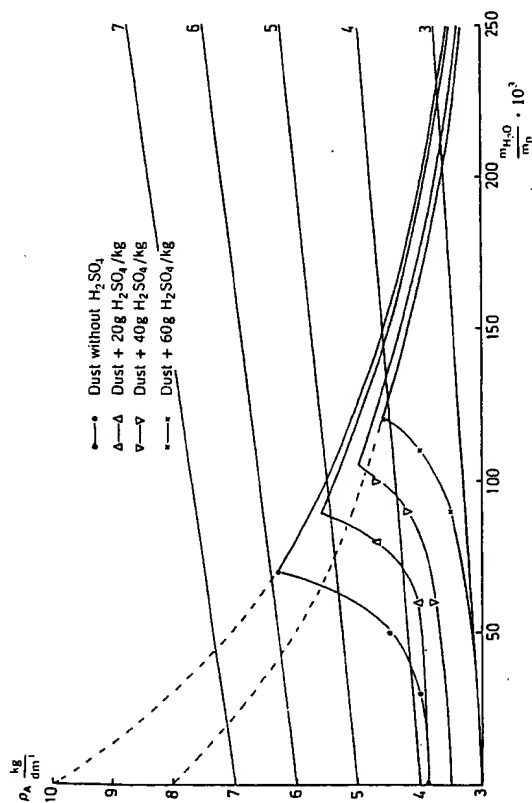


Figure 3.9 Apparent density of mill dust (I of Figure 2.58) as a function of sulfate content and water addition.

water are needed to reach the plastic states. Sekito and Ichimura (1968) showed that with other lead powders the width of the plastic range increases at low sulfate content (to about 3 to 4 kg/100 kg powder). With larger sulfate contents, that is, in pastes largely containing fibers of tribasic sulfate, the width of the plastic range becomes smaller and may completely disappear.

The preceding considerations naturally apply only if the basic sulfate forms as needles. If a strongly localized overacidification occurs, grainy normal lead sulfate is produced, a structure unfavorable to subsequent pasting.

Once a fibrous structure is obtained, it is retained in the curing process. The strength of the structure is improved because of the needle crystals. To ensure sufficient strength in the plates, synthetic fibers are often added to the highly porous active materials. In addition, tribasic sulfate increases the strength [Voss and Freundlich, patent (1965)].

During manufacture of the active materials for the negative plates, further additions are made (see Section 2.2) which may affect their rheological properties, mainly by changing surface tension and the contact angle of the organic components. There are no published data on this subject.

The pasting properties (i.e., their plastic behavior) are important in the manufacture of plates and also affect the electrochemical properties of the

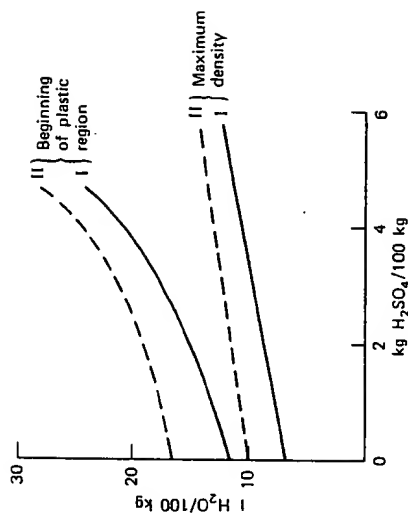


Figure 3.10 Dependence of the density maximum and beginning of the plastic range on the acid content of two mill dusts (I and II of Figure 2.58).

finished plates. During the grid loading the composition of the pastes forms the basis for the structure of plates and thereby determines the volumetric capacity.

No generalities may be made on a satisfactory paste density, for they do not unequivocally determine the behavior of the active material. However, the more porous an active mass, the larger the internal surface consequently a higher useful capacity and a better utilization is obtained. Yet the paste density or its water content is not a unique measure for the porosity, for the latter also depends on the active material structure after curing and formation. The shrinking process especially leads to different stabilities for the same paste densities that exert an effect on the life cycle.

Positive pastes with densities $\rho_p < 3.9 \text{ kg/liter}$ are less suitable, for they tend to sludge. For paste densities $\rho_p > 4.3 \text{ kg/liter}$ the capacities are smaller; also such dense materials often tend to warp.

Somewhat higher densities in the range $4.2 < \rho_p < 4.9 \text{ kg/liter}$ are recommended for the pastes of negative active masses.

RHEOLOGY OF THE CURING PROCESSES

After curing crackfree drying of the plates and thorough oxidation of the residual lead should be guaranteed. During curing the paste shrinks and contracts. Because contact with the grid rods and grid frames must not be lost, controlled or linear shrinkage, called capillary shrinkage because of withdrawal of water, is desired. It should proceed as a decrease in volume without additional void formation (see Section 2.6).

TABLE 3.7. TIME DEPENDENCE OF THE CURING PROCESS*

(1) Test Number	(2) Void Volume (V_v)	(3) Water Content V_w (100 w (H ₂ O))	(4) Void and H ₂ O- Volume ($V_v + V_w$)	(5) Change in Void Volume (ΔV_v)	(6) Change in H ₂ O- Volume (ΔV_w)	(7) Change of Total Volume (ΔV_A)	(8) Shrinkage Factor ($\Delta V_w/\Delta V_A$)	(9) Content of Metallic Pb [100 w (Pb)]	(10) Pore Diameter d (μ m)
Initial value	0.0	20.0	20.0					—	
1	0.4	19.0	19.4	0.4	-1.0	-0.6	1.7	18.0	20-30
2	0.9	14.0	14.9	0.5	-5.0	-4.5	1.1	17.3	
3	1.7	11.8	13.5	0.8	-2.2	-1.4	1.6	18.0	
4	3.0	9.1	12.1	1.3	-2.7	-1.4	1.9	17.8	11.2
5	4.2	8.6	12.8	1.2	-0.5	+0.7	0.7	17.9	3.2
6	9.0	3.9	12.9	4.8	-4.7	+0.1	47	10.5	1.9
7	10.2	2.8	13.0	1.2	-1.1	+0.1	11	10.6	0.34
8	11.5	1.0	12.5	1.3	-1.8	-0.5	3.6	10.3	0.24
Final value	12.5	0	12.5	1.0	-1.0	0		—	0.32

$$S_{\text{ideal}} = \frac{20 - 11.5}{20 + 11.0} = 0.27; S_{\text{real}} = \frac{20 - 12.6}{20 + 11.0} = 0.24 \text{ (for test No. 3)}$$

* All volumes are given in liters/100 kg, mass content in 100 w = weight %, solid volumes amount to 11 liter/100 kg.

To ensure drying without the formation of cracks, two steps in the process must be distinguished. In the first phase the liquid saturated paste undergoes a steady loss of water and decrease in volume so that no cracks or coarse pores form. This means that the density change must follow the same curve as the addition of water after the density maximum. If, after mixing, no additional chemical or physical changes occur in the paste, the maximum density will again be reached on completing this first phase. Because a portion of the lead has been oxidized, however, and a certain amount of recrystallization often occurs, a shift to smaller density values and therewith to higher porosities may be expected. At or near the maximum density is an aggregate of particles that mutually touch and support one another.

During the second phase of water removal no further volume changes may occur. The water is removed only when voids are formed. The density decreases linearly with the water content and the porosity remains constant, no matter whether or not the void space is filled with water. The mass fields are not allowed to detach from the grid. The total shrinkage should be limited to a decrease in thickness.

Table 3.7 describes the behavior of the curing process with time, during which samples were taken at about 2-hour intervals. This table describes a paste of a sulfate-containing powder whose water content at the maximum density $V_v = 0.115$ liter/kg; the specific solid volume is $V_s = 0.110$ liter/kg.

Table 3.7 contains the analytically determined content of metallic lead by weight (column 9), water V_w (column 3), and void volume V_v (column 2), determined from measurements with the Hg porosimeter. The decrease in interstitial volume ($V_v + V_w$) is recognizable during the first phase in sample 3, the values remain constant to completion of the processes (average value, 0.126 liter/kg). For ideal shrinkage no air-filled cavity should form during the first phase; eventually the interstitial void volume associated with the maximum density, 0.115 liter/kg will be attained. As Figure 3.11a shows, coarse cavities with pore diameters of more than 10 μ m (column 10) appear. The shrinkage factor (column 8) lies in the region of 1, the value for ideal shrinkage. According to the model, the removal of water from the fine pore system occurs inversely to the water take-up.

In the second phase of the process, beginning at sample 4, almost no change in total volume occurs. Usually a fine-pored cavity starts to form, as noted experimentally by the shift in the inflection point of the curves in Figure 3.11a from 3.2 to 0.3 μ m. In the logarithmic distribution curves of Figure 3.11b (for curves 6 and 8 of Figure 3.11a) show more clearly the existence of coarse and fine-pore voids.

At first the interstitial water is removed, and the residual wedge water is bound more firmly, by which a porosity extending through the entire material originates and air can penetrate in sufficient amounts through these pores.

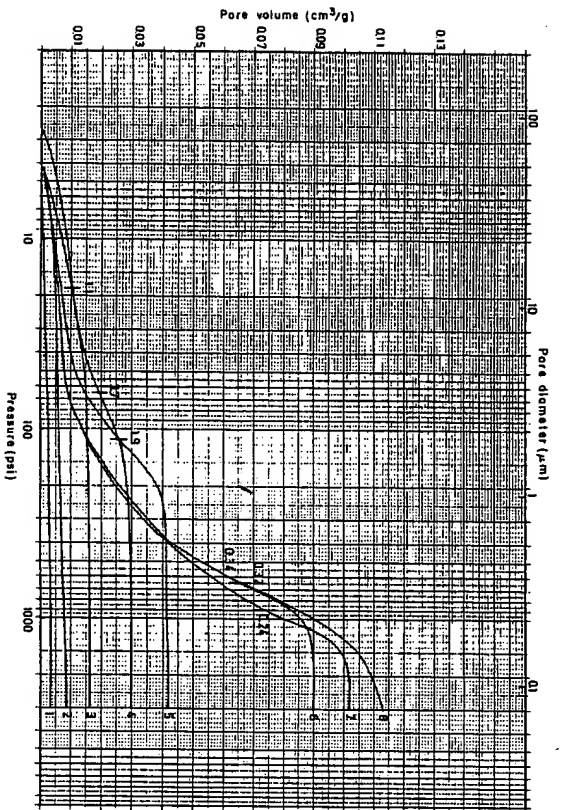


Figure 3.11a Mercury porosimeter measurements on unformed plates during the curing and drying process.

The particle surfaces are still covered with a thin film of water. Under this water film oxidation of lead occurs at a higher rate.

It is observed that the lead content decreases abruptly after sample 5 at a water content of about 8.6%. Although in this experiment a lower limit of about 10% by weight of metallic lead was reached in manufacturing, it must drop further.

According to Greenburg et al. (1951), a maximum of lead oxidation occurs at 5 to 5.5% (water, whereas Humphreys et al. (1970) give a somewhat higher value of 7.0 to 8.5% water content.

The heat generated during lead oxidation vaporizes the adsorbed and wedge water, the tightest bound portions. If the vaporization occurs too early or too rapidly, the oxidation of lead is hindered, for water is a catalyst in this process (see section 2.1). The temperature rise indicates the end of the curing processes. The dissolved material (also lead oxide) concentrates in the wedge water and deposits as a cement on the contact points of the particles. Newly precipitated lead oxide strengthens the network of needles which raises the dry strength of the plates.

The manufacture of crackfree plates is safest if the shrinkage is small, everything else being equal. On the other hand, there must be enough water

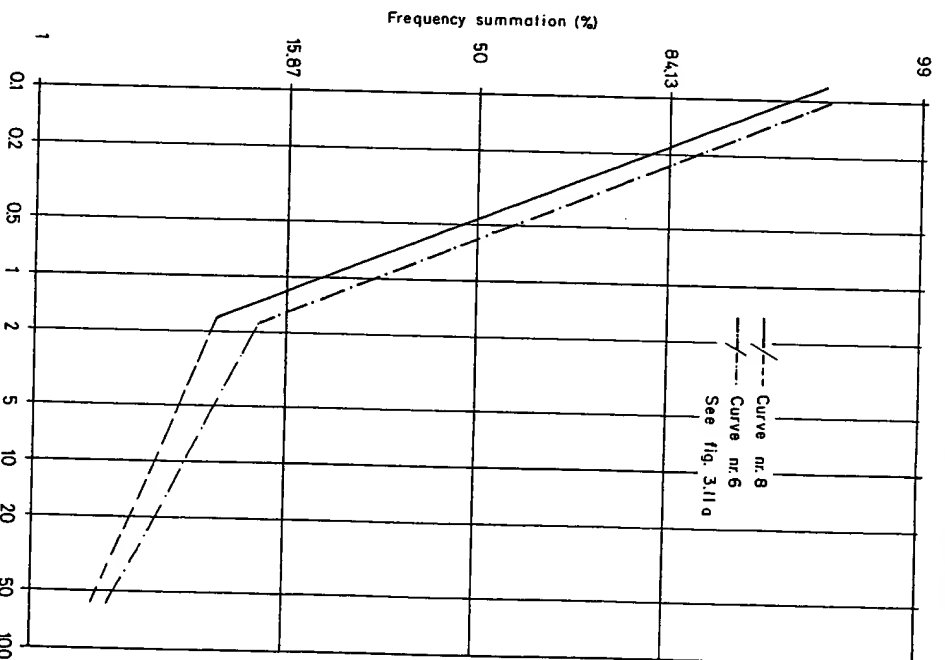


Figure 3.11b Replotting of curves 6 and 8 to show the logarithmic normal distribution.

present so that the material can be pasted and loaded in the grid and to give the plates enough porosity. Therefore the following conditions apply:

1. A lead powder is used with a high water value at the density maximum.
2. This value may be increased by the addition of sulfuric acid.
3. The water content is held as low as is compatible with the production techniques.

The first and third conditions are based on the characteristics of the dust. They are dependent on particle size distribution, shape, and internal surface. The second requirement is freely chosen for dusts within a certain range.

As a numerical example, Table 3.8 describes the behavior of a special lead dust. Its water absorption is given Figure 3.9. This dust has a water value of 0.10 liter/kg at maximum density. It was mixed in two sets of experiments:

1. At constant water content with variable amounts of sulfuric acid.
2. At constant sulfuric acid content with variable amounts of water.

The pasted grids are treated under constant conditions (15 hours in a humid atmosphere, followed by two days of air drying). Table 3.8 is a summary of paste properties as a function of water and sulfuric acid content.

1. The paste density is almost entirely independent of sulfuric acid content but is strongly affected by water content; see columns 4 and 5 in Table 3.8.
2. The solid volume changes only slightly with the sulfate content; see column 6 in Table 3.8 (on oxidation of lead from $W(Pb) = 0.30$ to < 0.05 , the volume increased by about $\Delta V_s = 0.01$).
3. The void formation during the curing process depends on the water content of the paste for equal working conditions; compare columns 1 and 7 in Table 3.8.
4. The more the water content of the paste exceeds the value V_{max} , the greater the tendency to form large pores and cracks [real or irregular shrinkage, column 9 compared with the ideal value in column 10].
5. In manufacturing the volume changes during shrinkage are essentially determined by the technology of the curing processes. Thus the total volume change (column 8) for the pastes of like water content ($W = 0.2$) is the same ($\Delta V_t = 0.058 \pm 0.002$), for they are worked under the same conditions. Mixtures that approach the ideal shrinkage show the largest value of maximum density.

Column 12 in Table 3.8 lists the relative portion of irregular shrinkage of the plates' total pore volume. The trend confirms the assumptions. Specifically, the numerical values apply only to a particular paste and to a definite curing and drying program. The quantitative behavior depends, among other factors, on the plate's thickness, temperature, and the moisture content in the manufacturing machines. Deviations may be caused by increasing the volume of the solid as a result of the oxidation of lead and the change in the fiber structure induced by recrystallization.

The curing process can be carried out by diversified methods, but several generalities must be considered. The first phase of the shrinkage in volume

TABLE 3.8. DEPENDENCE OF SHRINKAGE OF A LEAD DUST PASTE ON WATER AND ACID CONTENT^a

(1) Water Content V_w (%)	(2) H_2SO_4 g/l kg Pb- Dust	(3) Water Value at Maximum Density (liter/kg)	(4) Paste Density (kg/liter)		(6) Solid Volume ^b V_s (liter/kg)	(7) Void Volume V_v (liter/kg)	(8) Change in Total Volume ΔV_t (liter/kg)	(9) Shrinkage (vol %)		(11) $V_v - V_{max}$	(12) $\frac{V_v - V_{max}}{V_v}$
			Experimental	Calculated				S_{real}	S_{ideal}		
20	0	0.100	4.10	3.98	0.102	0.145	0.055	18.2	33.1	0.045	0.31
20	0.02	0.114	4.09	3.97	0.108	0.144	0.056	18.2	27.9	0.030	0.21
20	0.03	0.120	4.05	3.97	0.110	0.141	0.059	19.0	25.8	0.021	0.25
20	0.04	0.126	4.08	3.96	0.113	0.139	0.061	19.4	23.6	0.013	0.09
20	0.05	0.133	4.05	3.96	0.115	0.143	0.057	18.1	21.2	0.010	0.07
18	0.05	0.133	4.21	4.17	0.115	0.137	0.043	14.6	15.9	0.004	0.03
20	0.05	0.133	4.05	3.96	0.115	0.143	0.057	18.1	21.2	0.010	0.07
22	0.05	0.133	3.83	3.79	0.115	0.162	0.058	17.3	26.0	0.029	0.18
24	0.05	0.133	3.65	3.63	0.115	0.172	0.068	19.2	30.1	0.039	0.23

^a See Figure 3.9; V_{max} = maximum density.

^b Initial value with $W(Pb_{met}) = 0.30$; final value after oxidation $W(Pb_{met}) < 0.05$.

should occur during not too rapid drying in a damp atmosphere (vapor pressure slightly less than the vapor pressure of the water in the paste) at a low temperature (below 70°C). In the second phase drying should be completed without a change in volume.

The mixing and curing processes are important because they control the physical structure of the finished plates. The development of a compact structure is determined by kneading the mixture. Experimentally, the compact structure corresponds to maximum density, a coordination number of about 7, and between 40 and 60% porosity.

On transition from the maximum density to the plastic state, the particles are separated by a thin film of water without any appreciable change in structure. In the reverse process for removing water the same compact structure should be attained. This structure corresponds to maximum density and can be characterized by *maximum shrinkage*. Thus crack-free drying is accomplished and the plates possess a void volume with fine pores and a large internal surface.

OTHER COMPONENTS OF ACTIVE MASSES

The life and capacity of electrodes depends not only on the lead-containing components discussed in the preceding sections but also on other materials added deliberately or accidentally to the active materials of the plates.

The desired additives include expanders in the negative active material and fibers to raise the strength. The addition of phosphoric acid to the paste or electrolyte (see Section 2.1) leads to an increase in life by hardening the active mass but to a loss of capacity (Kugel, 1926/1929) and added difficulties if used at a low temperature. Other substances could be formed during battery use by dissolving impurities or alloy constituents in the grids, the antimony compounds in particular.

A third group contains a series of materials added to the electrolytes which somehow influences the behavior of the active masses of the electrodes — "secret substances" that are supposed to improve sulfated batteries. In many cases their action is disputed, often called worthless, and may even be harmful. A discussion of these materials is not provided here.

Characteristic of all these additions to the active materials is their use at low concentrations. They do not participate stoichiometrically in the electrochemical reactions but act as catalysts or inhibitors, mainly by changing the absorptive properties and structure of the electrical double layer.

Antimony

Cells with hard lead grids show the effect of antimony. Lead powder, however, also contains small amounts of antimony (about 10 to 100 ppm).

Therefore absolutely antimony-free cells are never encountered. The antimony content of lead dust occurs as an impurity in pure lead and accelerates the oxidation of lead in the mills and the Barton process.

During formation relatively large amounts of antimony dissolve from the positives (0.15% of the total antimony dissolves in 45 hours), whereas a small amount dissolves out of the negative grids, and only near completion of the formation (less than 0.01%). Formation was carried out with $\rho = 1.09$ kg/liter and $i = 0.35$ A/dm² of plates with hard lead grids (antimony content, 8%). Antimony was determined with radioactive ¹²⁴Sb. Most of the antimony is reprecipitated in the positive active material (0.13% based on the total active material), less in the negative plate (0.01% based on the active material); (see Hermann et al., 1957/1958).

On continuous charge (300 hr at 0.6 A/dm²) dissolved antimony rises to 6%. The same value is attained on cycle life test (discharge 1 hr at 1.8 A/dm², charge 5 hr at 0.4 A/dm², 100 charge/discharge cycles). The largest part is always deposited in the positive active material (up to 0.5%), and only about 0.03% in the negative active material (depending on cycling activity) but up to 1.2% on the overcharge test. The electrolyte may contain 3 to 15 mg/liter.

In the overcharging test the possibility of forming SbH₃ (based on the same amount of current under comparable conditions) appears to be greater than in the cycling test. Here, too, antimony is found mainly in the positive active material (up to 0.5%) (Zehender et al., 1964).

If antimony (as Sb₂O₃) is added in larger amounts (up to 10%) to lead dust, the oxidation of metallic lead is almost entirely prevented during the curing process (Ritchie, 1952).

The inhibiting action appears to be complex, for antimony is found in all states of oxidation, Sb^v, Sbⁱⁱⁱ, and Sb^o. The purpose of adding antimony oxide is related to the decreased life of plates with antimony-free grids. In particular, the sludging of the positives increases. Also, the difficulties that occur during curing make it unlikely that antimony in the grid will be replaced by the addition of oxide as long as metallic lead-containing dusts are used.

The electrochemical behavior of antimony in relation to the acidity and valence states is shown in Table 3.9 (see also Dawson et al, 1971). If metallic antimony is charged anodically in a sulfuric acid solution (without complex-forming components), starting from the potential of the standard hydrogen electrode, trioxide will form first. The pentoxide then forms with further rising potential. If these oxides are present as precipitates, the concentrations of the dissolved antimony are fixed. In solution we find trivalent antimony as antimonyl (III) ion (SbO)⁺ and undissolved antimony (III) acid (HSbO₂). The pentavalent antimony (V) occurs as (SbO₂)⁺ and the antimonic (SbO₃)⁻.

A STUDY OF SOME OF THE CRYSTALLOGRAPHIC AND MICROSCOPIC ASPECTS OF THE CURING OF POSITIVE LEAD-ACID BATTERY PLATES

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ABSTRACT

The process of curing or conditioning pasted lead-acid battery plates made with uncalcined or leady Barton pot litharge is probed. Microscopy, wet chemistry and X-ray diffraction techniques are used to characterize the changes in crystal structure and chemical composition which take place in the material as it undergoes curing.

A matched set of uncured positive plates is divided into groups each of which is then cured under different controlled conditions. At various times throughout the cure cycle, sample plates from each group are analyzed for composition and crystal structure. Photomicrographs used in conjunction with X-ray diffraction patterns illustrate the reactions which occur.

The plates cured under various conditions are then formed or charged. Time-lapse photographic techniques are used to follow the conversion of divalent lead compounds into the various species of lead dioxide. The degree of completion of formation and the proportions and characteristics of the two polymorphs of lead dioxide present in the formed plates of varying cure history are discussed.

INTRODUCTION

Interest in the crystallographic nature of the positive and negative active material in lead-acid battery plates has been stimulated in recent years by the extremely interesting and comprehensive reports generated at the U.S. Naval Research Laboratory. The microscopic studies of A. C. Simon and the X-ray diffraction techniques of J. Burbank are particularly noteworthy. The publications released by these researchers have proven to be invaluable references for anyone seriously interested in investigating the crystallographic characteristics at various stages of battery plate processing and life. Much of the work reported upon in this paper had its origin in findings published by NRL personnel.

BACKGROUND

Uncalcined or leady litharge has been utilized in the manufacture of paste for lead-acid battery plates for 25 years or more. This material,

was analyzed for moisture and metallic lead content. The progress of these two reactions as a function of time in a typical load is illustrated in Fig. 1. The two reactions occur simultaneously and complement each other since water is a necessary catalyst in the exothermic metallic lead oxidation and heat is required to evaporate the moisture from the plate.

To determine the manner in which the metallic lead is distributed and the way in which it reacts, metallurgical specimens were prepared for microscopic examination. Sample plates at various stages of cure were thoroughly dried and impregnated with epoxy resin under a vacuum. Upon hardening, the samples were cross sectioned, ground and polished. The procedures and equipment for sample preparation and microscopic observation were those introduced by Simon⁽¹⁾ with only slight modification by the author as previously described.⁽²⁾

Examination of the mounted, uncured plate segments revealed that the metallic lead particles in plates made with Barton pot type oxide are generally spherical in shape and vary in size from under a micron to about 50 microns in diameter. Partially cured plate segments (Figs. 2 and 3) exhibited particles of lead in an incompletely oxidized state. The centers of the original lead particles remained metallic at this stage while the outer portions have undergone oxidation. As might be expected, very few unreacted metallic lead particles were observed in the fully cured samples.

Another important aspect of the curing reactions—the oxidation or corrosion of the periphery of the grid bars—was not evident in samples

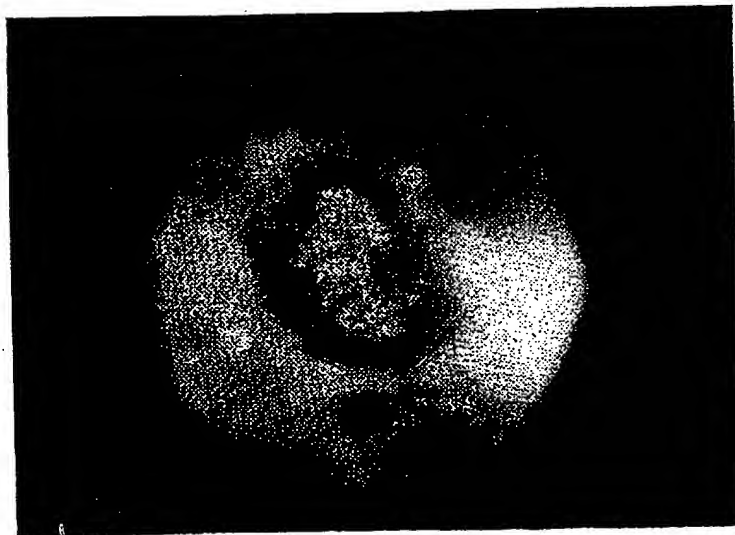


FIG. 2. Partially oxidized particle of metallic lead.

bars which results from this reaction improves the bond between the grid and the adjacent paste and, hence, strengthens the plate.

Basic Lead Sulfate Reaction

The next series of laboratory experiments undertaken was programmed to determine the effect of various curing parameters (temperature and humidity) on the curing reaction rates and on the crystallography of the cured plate.

Freshly pasted, uncured positive plates were placed in a controlled environment chamber and allowed to cure. Sample plates were removed after various cure durations, analyzed, mounted and polished as described above. The temperature within the chamber was varied between 100°F and 200°F and the relative humidity between 20 and 100 per cent.

Plates cured in the lower relative humidity range (<80 per cent) tended to dry out quickly leaving large quantities of unoxidized metallic lead. To avoid this condition, 100 per cent relative humidity was established as a standard for all subsequent curing experiments.

As the cure temperature was increased beyond 100°F, very little improvement in the rate of oxidation was noted; however, a change in at least one physical property—color—was quite obvious. Plates cured at temperatures below about 150°F changed very little in color—retaining their original yellowish-beige color throughout the cure cycle. Plates cured above this temperature, however, turned orange or reddish-orange by the time they were completely cured—the higher temperatures producing the darker colors. The color change could not be attributed directly to the oxidation of lead because virtually all of the metal was oxidized during the curing of the light as well as the dark plates. The color of plates cured at high (180°F) and low (120°F) temperatures as a function of time, measured with a reflectance colorimeter is indicated in Fig. 5. The high temperature curve shows a gradual darkening of the plate beginning at a cure time of approximately 10 hr, followed by an abrupt point of inflection (darkening) after about 20 hr of curing and then a levelling off from a cure time of 24 hr on. X-ray diffraction equipment was used as a supplementary tool to the microscope in determining the crystallographic significance of the high temperature color change.

The X-ray diffraction patterns, as traced by a diffractometer, identified the materials present in the uncured plates as metallic lead, lead monoxide (tetragonal), lead monoxide (orthorhombic), and tribasic lead sulfate hydrate ($3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$). The low-temperature-cured (light colored) plate contained the same compounds throughout curing, but, of course, the amount of metallic lead present diminished with increasing cure time. Diffraction patterns of the high-temperature-cured positive material began to show peaks for another basic sulfate—tetrabasic lead sulfate ($4\text{PbO} \cdot \text{PbSO}_4$)—

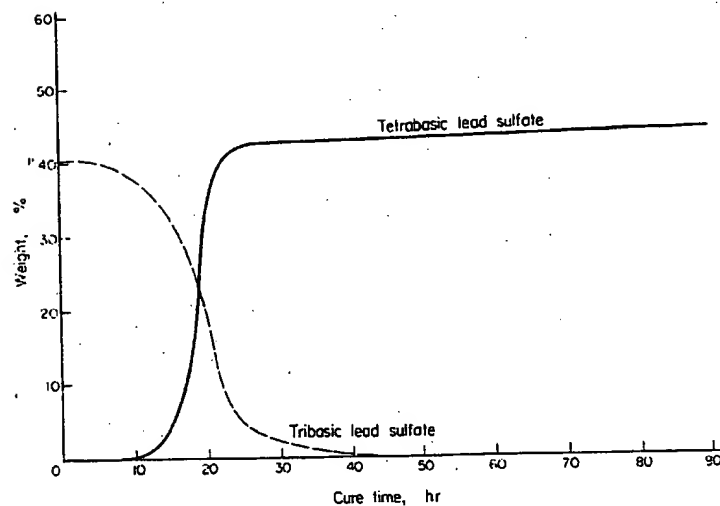


FIG. 6. Basic lead sulfate content versus cure time.

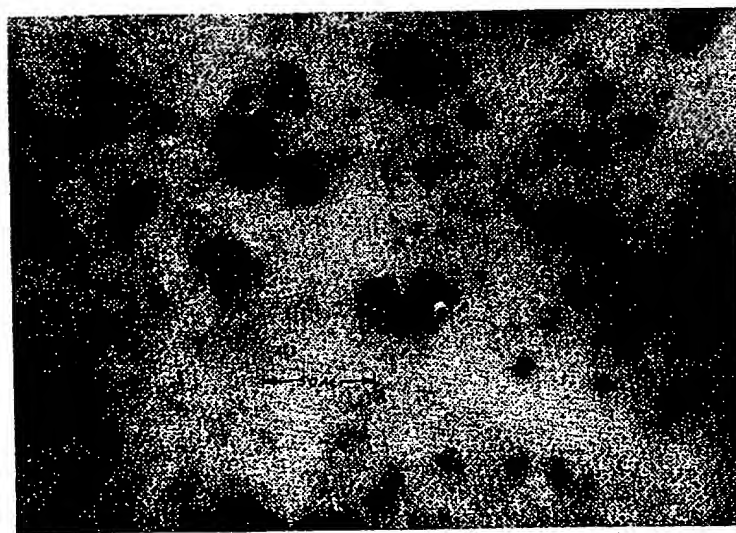


FIG. 7. Microstructure of positive paste—cure time 0 hr (180°F cure).

specimens taken after 10 hr of high temperature curing (Fig. 8) began to exhibit some large, coarse, dark-colored crystals. After 24 hr of high-temperature curing, the plate was comprised almost exclusively of very

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EXPERIMENTAL FORMATION

Several sets of cured positive plates (three to five plates per set) representing the various compositions and crystal structures were electrochemically formed to determine the effect of the two basic sulfates on the electrochemical properties of the plate. The plates to be formed were placed in transparent plastic cells so that the visible formation progress of the positive plates could be observed and photographed. The plates were connected in series and formed at the 20-hr rate (1.6 A) using a constant current, direct current power supply. Standard production negative plates, of identical weight and density, from a single mix were used as the counter electrodes and 1.050 specific gravity sulfuric acid as the electrolyte.

Photographic Technique

A 35-mm half-frame camera, mounted on a tripod and equipped with a spring-driven film-advancing motor, was used for photographing the formation progress. A cam-timer was employed to trigger automatically the camera's shutter and photograph the positive plates in the cells each hour during the formation. The timer was programmed for the following sequence: (1) turn the two photoflood lamps on; (2) activate the solenoid which, in turn, pneumatically advances the cable release plunger, thus opening the shutter and taking the photograph; (3) deactivate the solenoid thus pneumatically withdrawing the plunger, advancing the film to the next frame and cocking the shutter for the next picture; and (4) turn the photoflood lamps off. With this automated set-up no attendant was required. High-speed color reversal film was used and the resulting positive slides and color prints were compared in sequence.

Experimental Formation No. 1

The three positive plates shown in Fig. 10 originated in a single batch of paste. The light-colored (yellowish-beige) one at the left was cured at 120°F for 48 hr and contains no tetrabasic lead sulfate. The center plate, which is yellowish-orange, was cured at 150°F for 48 hr and is comprised of both tribasic and tetrabasic lead sulfate. The right-hand plate (dark reddish-orange) was cured for 48 hr at 180°F and all of its lead sulfate is in the tetrabasic form—no tribasic lead sulfate was detected in this sample. The curing of all three plates was carried out in a 100 per cent relative humidity atmosphere.

The three plates were formed in individual cells and the progress photographed as described above. Figure 10 shows the three positive plates at the start of formation. In Figure 11 the plates have been formed for 5 hr and the originally dark-colored, right-hand plate exhibits more darkened area (PbO_2) than either of the other plates. This trend became even more

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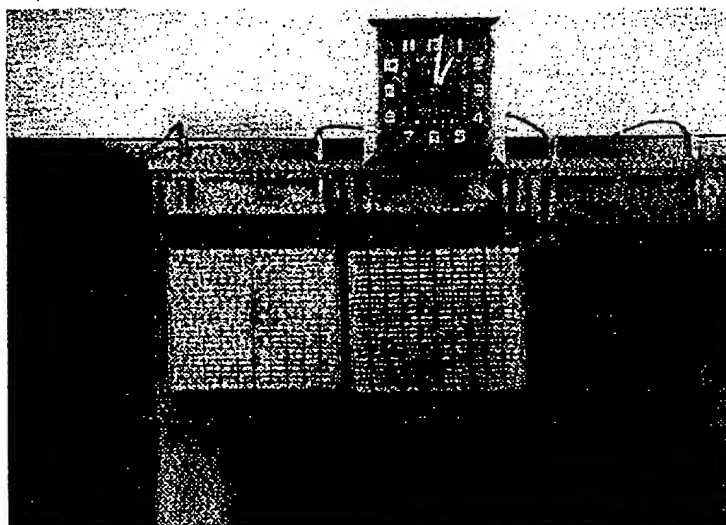


FIG. 12. Formation of positive plates of varying cure history—formation time 10 hr.

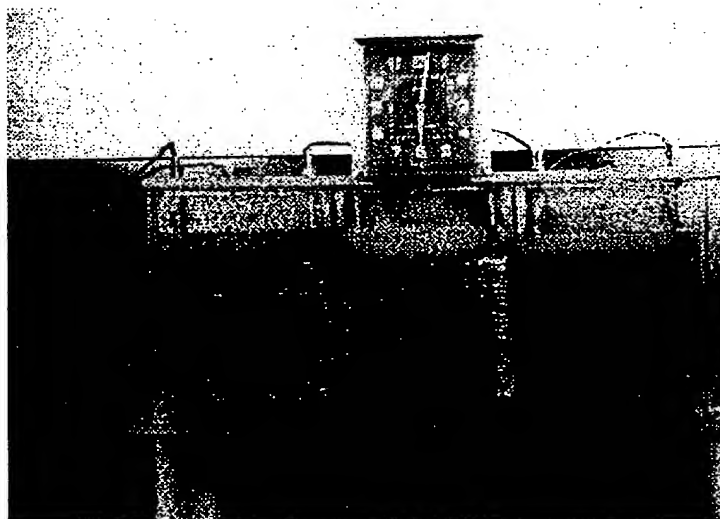


FIG. 13. Formation of positive plates of varying cure history—formation time 15 hr.

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The subsequent microscopic examination of the metallurgically prepared samples served to confirm the analytical results and to characterize more completely the crystallographic nature of the formed positive active material.

TABLE I. FORMED POSITIVE PLATE COMPOSITION
EXP. FORMATION No. 1

Plate No.	Unformed color	% PbO ₂	% α -PbO ₂
43° 1 (left)	Yellowish-beige	80.0	23.0
66° 2 (center)	Yellowish-orange	71.5	28.7
72° 3 (right)	Reddish-orange	52.4	36.4

The formed sample representing the originally light-colored positive plate appeared to be almost completely converted to finely divided lead dioxide and a good share of the lead dioxide was of a reddish-brown color indicating a preponderance of beta lead dioxide.



FIG. 15. Microstructure of high-temperature cured positive paste after formation.

Examination of the formed positive material originating from the dark reddish-orange unformed plate revealed quite a different structure. The majority of the coarse crystals which made up this specimen appeared to be incompletely formed. The peripheries of the large tetrabasic lead sulfate crystals were converted quickly to lead dioxide giving the outward appear-

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When a positive plate undergoes high-temperature curing ($>150^{\circ}\text{F}$), the finely divided crystals of tribasic lead sulfate present recrystallize as large, coarse crystals of tetrabasic lead sulfate. This recrystallization is generally accompanied by a change in plate color from a yellowish-beige to a dark reddish-orange.

Plates which contain a significant quantity of the large tetrabasic lead sulfate crystals appear to convert very rapidly to lead dioxide on formation. Actually the electrochemical conversion to lead dioxide is only superficial since the formation does not penetrate into the centers of the crystals. The ramifications of this type of incomplete formation should be quite apparent to those familiar with battery manufacturing and testing.

First, since only slightly more than half of the material (52.4 per cent) in the high-temperature-cured plates is actually converted to useable lead dioxide and a large portion of that (36.5 per cent) is in the lower capacity alpha-PbO₂ form, initial yields or efficiencies for a battery containing this type of plate would be extremely low.

Secondly, on subsequent cycling, more of the interior of these crystals would be converted to lead dioxide thereby releasing additional sulfate ions. This would lead to high electrolyte specific gravity and uneven gravities or concentrations from one cell to the next.

Both of the above effects were verified by assembling and testing batteries containing plates cured at elevated temperatures.

Tetrabasic lead sulfate crystals and the lead dioxide crystals which they are converted to during formation *do* have some desirable characteristics. The surface of these crystals forms very rapidly and serves to distribute the formation current throughout the plate. The size and high density of the crystals also would appear to enhance the mechanical strength of the material. If recrystallization of the basic sulfates can be regulated such that the quantity, shape and distribution of these crystals is optimized, it should be possible greatly to improve the efficiency and strength of the positive active material during formation and subsequent cycling.

Another approach designed to take full advantage of the crystallographic transformation would be aimed at methods for more completely converting the centers of the crystals to lead dioxide—preferably the higher capacity beta polymorph. This would result in a cellular structure with a hard, dense, conductive outer layer surrounding a high-capacity, finely divided central portion. This type of structure, if obtainable, would closely resemble that which Simon⁽⁴⁾ noted and Burbank⁽⁵⁾ characterized in examining long-lived positive lead-acid submarine battery plates.

The original photographs were in color and some of the contrast and resolution has naturally been lost in conversion to black and white prints for publication.

the orthorhombic or the tetragonal oxide which was preferentially "absorbed" into the tribasic sulfate. This would help resolve a perennial question which is raised among battery people. The orthorhombic is less reactive than the tetragonal form.

J. R. PIERSON: This, perhaps, is one of the things that prompted Mr. Crow's question on a very convenient way to determine the answer to your question. It would be very simple to make a high orthorhombic lead oxide with the Barton system and compare it with a tetragonal oxide from the ball mill system. The question has arisen in my mind but I haven't resolved it yet.

J. P. G. FARR (*Metallurgy Dept. University of Birmingham*): In connection with the question by Dr. S. C. Barnes concerning the production of PbO_2 from tetrabasic sulfate during formation, observations made by G. W. Greene and myself on the corrosion of the positive plate during service may be relevant. In a thin corrosion layer adjacent to the grid are found basic sulfate (in particular $4PbO \cdot PbSO_4$) and retained antimony. This suggests corrosion under conditions of reduced acidity (cf. curing). In a thicker, outer corrosion layer is found PbO_2 (90% α , 10% β). Antimony is removed from the initial layer in its transformation to the second layer. The latter thickens during service life, suggesting that it is comparatively unreactive electrochemically. If this thicker layer were converted to $PbSO_4$ on discharging then, following Burbank (*J. Electrochem. Soc.* 106 (1959), 369) and Bagshaw and Wilson (*Electrochem. Acta* 10 (1965), 867), one would expect βPbO_2 to be formed on recharging. The initial corrosion layer is up to 10μ in depth. It was characterized by electron diffraction using an A.E.I. EM6 electron microscope modified to give an expanded camera constant. This technique, which allowed basic sulfates to be distinguished, is to be published (B. Duggan and G. W. Greene, *J. Roy. Microscopical Soc.*, 1968).

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